EUROPEAN SYNCHROTRON RADIATION FACILITY

INSTALLATION EUROPEENNE DE RAYONNEMENT SYNCHROTRON

Experiment Report Form

	Experiment title: Structural reordering and crystallization of bulk metallic glasses probed by X-ray diffraction during in-situ fast calorimetry	**Experiment number**: MA-4660
Beamline: ID13	**Date of experiment**: from: 07.07.2021 to: 12.07.2021	**Date of report**: 25.02.2021
Shifts: 9 + 9	**Local contact(s)**: Jiliang Liu , Manfred Burghammer	*Received at ESRF:*

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Report:

Using high flux microfocus X-ray diffraction (XRD) during ultra-fast calorimetry from low temperatures up to the thermodynamic melting, changes in the glassy structure, as well as the formation of crystal nuclei, can be systematically studied. Different heating rates allow the supression of kinetically controlled processes as nucleation and growth of unwanted crystalline phases of the metallic glass. In situ XRD investigations at high heating rates of BMGs with maximum temperatures up to 1000 °C and to apply heating and cooling rates up to 100.000 Ks^{-1} on glassy material that due to a deep eutectic composition allows to be molten and quenched in-situ on the beamline to study the structural changes. The Beamline ID 13 has outstanding focussing abilities that allow to resolve the micron sized sample size used in chip calorimetry. The fast and high resolution Eiger pixel array detector allow for sampling rates of 750 fps, allowing to relsove in-situ fast changes in the material. A commercial Mettler Toledo Flash DSC 2+ device (FDSC) with a tailored break-out set-up for the high temperature (1000°C) UFH 1 semiconductor sensors was used for the thermal treatment and calorimetric measurements.

In the present experiment the challenges were to fully use the ability to apply complex measurement programmes involving heating and cooling at high rates while monitoring the structural changes with the full time resolution. Therefore it turned out that measurement times of up to 70 s lead to data storage issues in the ESRF network (buffering issue related to the high data acquisition rate). The support of the ESRF staff allowed to resolve these issues after several days. Furthermore, the resonance between the flash calorimeter and the beamline leads to lower quality of the FDSC data. In the end one day of beamtime could be used to acquire data allowing to derive full time temperature transition information (TTT) from both, the structural as well as from the calorimetric side. Figure 1 shows a TTT diagram of a Zr-based metallic glass AMZ4 recorded by an *in situ* FDSC. The alloy was previously characterised *ex situ* by Sohrabi *et al.* (2021) and in this experiment we managed to support the calorimetric measurement by real time diffraction data.

Inspite of the challenges in data acquisition large amounts of data were acquired for several metallic glass systems. The experience gathered during the experiment can be considered as a breakthrough in fast assessment of metallurgical phase formation for metallic alloys for fast and medium rate heat treatments as the full phase formation behavior can be assessed within second from both calorimetric and the structural viewpoint. We were also able to quantify the extent of beam damage in an organic sample by measuring the absorbed beam energy using the *in situ* FDSC set-up and qualitatively observe the sample degradation manifested by changes in the characteristic peaks in FDSC heating curves. These measurements are equally relevant for metastable metallic phases, e.g. metallic glasses.

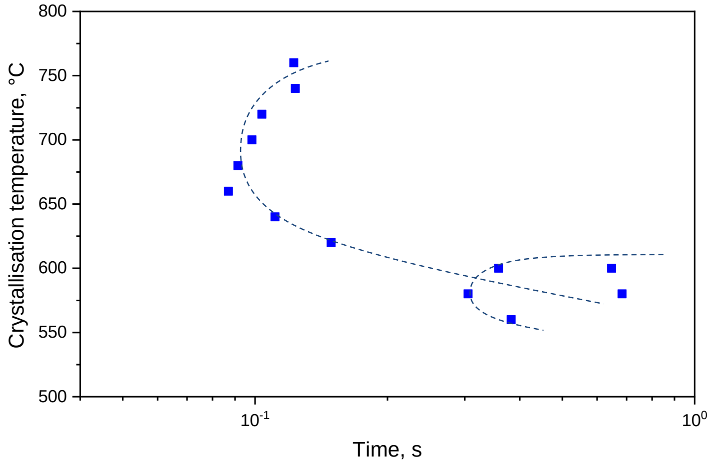

Figure 1: Peak temperatures of the crystallisation peaks measured upon cooling of the AMZ4 Zr-based alloy measured in the beam. Corresponding diffraction patterns were acquired.